

APS

X-ray Biogeochemistry: Elucidating Bacteria–Mineral–Contaminant Interactions at the Molecular Scale

M. Boyanov¹, E. O'Loughlin¹, D. Sholto-Douglas¹, K. Skinner¹, M-J. Kwon¹, B. Mishra¹, K. Fletcher², F. Loeffler², M. Marshall³, J. Fredrickson³, T. Shibata⁴, B. Lai⁴, and K. Kemner¹

¹Biosciences Division, Argonne National Laboratory, Argonne, IL 60439, USA

²Civil & Environmental Engineering, Georgia Institute of Technology, Atlanta, GA 30332, USA

³Biological Sciences Division, Pacific Northwest National Laboratory, Richland, Washington 99352, USA

⁴Advanced Photon Source, Argonne National Laboratory, Argonne, IL 60439, USA

The selection of waste repository sites and the design of remediation strategies require a good understanding of radionuclide contaminant transport in subsurface environments. Macroscopic parameters of interest such as concentration profiles or propagation rates are ultimately controlled by the molecular interactions between the dissolved ions and the mineral and/or biological phases along the flow path. In addition to passive processes such as surface sorption, the solubility of contaminants is strongly influenced by redox transformations caused by metabolizing bacteria or their products. The interplay between biotic and abiotic factors creates a complex reaction network that is actively being studied with the goal of building a predictive computational model.

This presentation will review several important molecular-scale processes that control uranium solubility in the subsurface and present case studies where X-ray absorption fine structure (XAFS) spectroscopy and X-ray fluorescence (XRF) nano-spectroscopy at the Advanced Photon Source were instrumental in providing the insight necessary for understanding observed contaminant behavior. In one such study of uranium reduction by bacteria, XRF spectroscopy at submicron spatial resolution was able to show co-localization of uranium precipitates and biological material in the extracellular space, implicating outer-membrane proteins (cytochromes) in the extracellular reduction of uranium. In another study, X-ray absorption near-edge spectroscopy (XANES) at submicron spatial resolution was able to show heterogeneity in the valence state of uranium relative to the position of single bacteria on a thin iron oxide film. In a third study of U(VI) reduction, we show how a combination of biotic and abiotic experiments provides insight on mineral nucleation near organic surfaces and leads to the discovery of unexpected U(IV) phases that may have very different transport properties than the usually assumed uraninite phase. These studies highlight the importance of molecular scale information in understanding macroscale processes and the need for improvements in the techniques used to access this information.